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Ionic conductivities of non-equivalent molten salts by molecular dynamics simulations

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これまで我々は等価溶融塩のイオン伝導度について検討してきたが、本研究は理論面での非等価溶融塩への拡張である。イオン伝導度は速度相関関数および二体ポテンシャルで表され、また Langevin 方程式を用いてイオン伝導度の比 σ^+/σ^- が $|z^+| m^- / |z^-| m^+$ に等しいことが示された。これは等価溶融塩の場合の逆質量比の関係の非等価溶融塩への拡張となっている。また、溶融 CaCl_2 及び AlF_3 についての理論の計算結果とシミュレーションの良好一致を得た。

This is a serial work on the theoretical derivation of the partial conductivities in various type molten salts. In previous papers, we have carried out the theoretical treatment for the electrical conductivities of equivalent molten salts and their mixtures, starting from generalized Langevin equation for cation and anion in these systems and using Kubo-Green formula with the help of various velocity correlation functions between a chosen pair of ions in them [1,2,3]. From these, one of the obtained important results is that the ratio of partial conductivities of cation and anion in a pure equivalent molten salt, σ^+/σ^- is always equal to their inverse mass ratio m^-/m^+ . It is interesting to know how the golden rule $\sigma^+/\sigma^- = m^-/m^+$ is modulated in such non-equivalent molten salts. $M^{2+}Y^{1-}$ -type molten salt and $M^{3+}Y^{1-}$ -type molten salt are concerned as the non-equivalent ones. Practical molten salts corresponding to these types are, e.g., CaCl_2 , which is useful for an industrial chemistry extracting metallic Ca. Taking account of another industrial applications, molten AlF_3 seems also to be useful for extracting metallic aluminum. At first, we derive the partial conductivities of $M^{2+}Y^{1-}$ -type molten salt from microscopic point of view based on the Kubo-Green linear response theory using a simplified Langevin equation. The starting Langevin equation for either cation M or anion Y is written as follows [4],

$$m^\pm (dv_i^\pm(t)/dt) = -m^\pm \gamma^\pm v_i^\pm(t) + z^\pm e \varepsilon_i(t) + z^\pm e E \quad (1)$$

where m^\pm is the ion's mass, $v_i^\pm(t)$ is the ion's velocity at the time t , γ^\pm is the effective friction constant acting on either cation or anion, z^\pm is the ion's charge, $\varepsilon_i(t)$ is the random fluctuating force acting on ion i , and E is the applying external field. If we assume that this force at time t , is not influenced by its former or later time t' ($\neq t$), then we have

$$\langle \varepsilon_i(t) \varepsilon_i(t') \rangle = \alpha \delta(t-t') \quad (2)$$

where α means the strength of random fluctuating field. Using (1) and

(2), then we have the following ensemble averages,

$$\langle v_i^{\pm 2}(t) \rangle = (\alpha z^{\pm 2} e^2 / 2 m^{\pm 2} \gamma^\pm) \quad (3)$$

According to the equi-partition rule, we have

$$(1/2) n^+ m^+ \langle v_i^{+2}(t) \rangle + (1/2) n^- m^- \langle v_k^{-2}(t) \rangle = (3/2) n k_B T \quad (4)$$

where n is defined as $n = n^+ + n^-$.

Combine (1) and (4), then α is expressed as,

$$\alpha = \{ (3/2) n k_B T \} / [(n^+ z^{+2} e^2 / 4 m^+ \gamma^+) + (n^- z^{-2} e^2 / 4 m^- \gamma^-)] \quad (5)$$

Equation (1) can be extended to the current density $j^\pm(t)$ with the mean random fluctuating field $\varepsilon(t)$, instead of $v_i^\pm(t)$ and $\varepsilon_i(t)$, as,

$$j^\pm(t) = \sum_{i=1}^{n^\pm} z^\pm e v_i^\pm(t) \quad (6)$$

and

$$\varepsilon(t) = (1/n) \sum_{i=1}^n \varepsilon_i(t) \quad (7)$$

then we have,

$$\begin{aligned} \langle \varepsilon(t) \varepsilon(t') \rangle &= (1/n^2) \sum_i^n \langle \varepsilon_i(t) \varepsilon_i(t') \rangle = (\alpha/n) \delta(t-t') \\ &= 6 k_B T \delta(t-t') / [\{ (n^+ z^{+2} e^2 / m^+ \gamma^+) \} + \{ (n^- z^{-2} e^2 / m^- \gamma^-) \}] \end{aligned} \quad (8)$$

Taking similar treatments as [1], then we have,

$$j^\pm(t) = (n^\pm z^{\pm 2} e^2 / m^\pm \gamma^\pm) \varepsilon(t) \quad (9)$$

On the other hand, the Kubo-Green type representations for partial conductivities are given as follows, [1,2,3]

$$\sigma^\pm = (1/3 k_B T) \int_0^\infty \langle j^\pm(t) j(0) \rangle dt = n^\pm z^{\pm 2} e^2 / m^\pm \gamma^\pm \quad (10)$$

where $j(t)$ is equal to $j(t) = j^+(t) + j^-(t)$.

By Taylor expansion of second term of (10) and some algebraic manipulations, we have for CaCl_2 , [5]

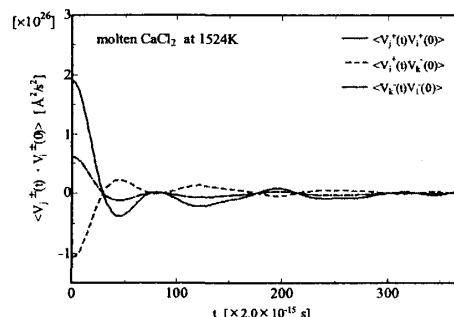


Fig.1 Velocity correlation functions of molten CaCl_2 at 1524K.

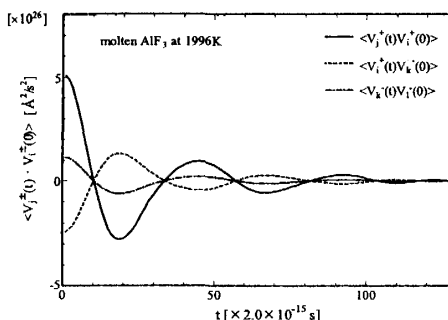


Fig.2 Velocity correlation functions of molten AlF_3 at 1996K.

$$\sigma^{\pm} = (n^{\pm} z^{\pm} e^2 / m^{\pm}) \int_0^{\infty} [1 - \{ (t^2/2) (2n_0 \langle \phi^{\pm} \rangle / 9\mu) \} + (\text{higher order})] dt \quad (11)$$

where

$$\langle \phi^{\pm} \rangle = \int_0^{\infty} \{ (\partial^2 \phi^{\pm} / \partial r^2) + (2/r) (\partial \phi^{\pm} / \partial r) \} g^{\pm}(r) 4\pi r^2 dr \quad (12)$$

and μ is the reduced mass of CaCl_2 ,

$$1/\mu = (2/m^+) + (1/m^-) \quad (13)$$

In (12), ϕ^{\pm} is the inter ionic potential between anion and cation.

Comparing the third term of (10) and (11), we have,

$$1/\gamma^{\pm} = \int_0^{\infty} \{ 1 - (t^2/2) \gamma^{\pm 2} + (\text{higher order}) \} dt \quad (14)$$

We take $n^+ = n_0$ and $n^- = 2n_0$ for CaCl_2 , then,

$$\gamma^{\pm} = (2n_0 \langle \phi^{\pm} \rangle / 9\mu)^{1/2} \quad (15)$$

Then as the consequent, we have the relation, as,

$$\gamma^+ = \gamma^- \equiv \gamma \quad (16)$$

Therefore, we have the conductivity ratio, as,

$$\sigma^+ / \sigma^- = |z^+| m^- / |z^-| m^+ \quad (17)$$

where $|z^+| = +2$ and $|z^-| = -1$ for molten $\text{M}^{2+}\text{Y}^{1-}_2$ salts. The equation (17) is the extension of the relation $\sigma^+ / \sigma^- = m^- / m^+$ for equivalent binary salts to that of non-equivalent system. For molten AlF_3 , we can ascertain the same relation as (17) is valid, where $|z^+| = +3$ and $|z^-| = -1$.

Further consideration for conductivity coefficient, we have,

$$\sigma^{++} / \sigma^{+-} = \sigma^{+-} / \sigma^{--} = |z^+| m^- / |z^-| m^+ \quad (18)$$

$$\sigma^{++} / \sigma^{--} = |z^+|^2 (m^-)^2 / |z^-|^2 (m^+)^2 \quad (19)$$

On the other hand, according to the momentum conservation law, it is straightforward to obtain the cross velocity correlation functions for molten CaCl_2 , as,

$$\langle v_j^+(0) v_i^+(0) \rangle = -(2m^- / m^+) \langle v_i^+(0) v_k^-(0) \rangle \quad (20)$$

$$\langle v_k^-(0) v_i^-(0) \rangle = -(m^+ / 2m^-) \langle v_i^+(0) v_k^-(0) \rangle \quad (21)$$

$$\langle v_i^+(0) v_k^-(0) \rangle = -9k_B T / (m^+ + 2m^-) \quad (22)$$

For molten AlF_3 , we obtain the following relations, as,

$$\langle v_i^+(0) v_j^+(0) \rangle = -(3m^- / m^+) \langle v_i^+(0) v_k^-(0) \rangle \quad (23)$$

$$\langle v_k^-(0) v_i^-(0) \rangle = -(m^+ / 3m^-) \langle v_i^+(0) v_k^-(0) \rangle \quad (24)$$

$$\langle v_i^+(0) v_k^-(0) \rangle = -12 k_B T / (m^+ + 3m^-) \quad (25)$$

In order to confirm above results, we perform the molecular dynamics (MD) simulations in non-equivalent molten binary salts, CaCl_2 and AlF_3 . Tosi-Fumi type pair potentials are used in MD, which are expressed as,

$$V_{ij}(r) = Z_i Z_j e^2 / r + B_{ij} \exp(-a_{ij} r) - C_{ij} / r^6 \quad (26)$$

where the used potential parameters are taken from literature. The obtained pair distribution functions agree well with experiments or previous MD results. As is treated so far, the relations between velocity correlation functions are expected, i.e. (20), (21) and (22) for CaCl_2 . For AlF_3 , (23), (24) and (25) are applied. To confirm the validity of these relations, we calculate the velocity correlation functions as the functions of time. The results are shown in Fig.1 and Fig.2. Obviously seen in these figures, three velocity correlation functions oscillate with same phase, and the ratios of absolute value of them at arbitrary time t is in the same ratios as at $t=0$. The correlation functions at $t=0$ obtained by the theory and MD agree well within the error about 4%.

Fig.3 and Fig.4 show the current correlation functions of molten CaCl_2 and AlF_3 as functions of t , respectively. The graphs in Fig.3 and Fig.4 are normalized by $\langle j^-(0) j^-(0) \rangle$. From these results, the relation between the current correlation functions are numerically confirmed to be constant, as,

$$\langle j^+(t) j^+(0) \rangle / \langle j^-(t) j^-(0) \rangle = \langle j^+(0) j^+(0) \rangle / \langle j^-(0) j^-(0) \rangle = |Z^+| m^- / |Z^-| m^+ \quad (27)$$

The ratios of the current correlation functions obtained by MD are 1.769 and 2.112, for CaCl_2 and AlF_3 , respectively. The agreement with the theory is excellent. According to [2], the correlation functions have the same decaying form with time, which we write as $f(t)$, then we have,

$$\sigma^{++} / \sigma^{+-} = \{ \langle j^+(0) j^+(0) \rangle \int_0^{\infty} f(t) dt \} / \{ \langle j^-(0) j^-(0) \rangle \int_0^{\infty} f(t) dt \} = \langle j^+(0) j^+(0) \rangle / \langle j^-(0) j^-(0) \rangle = |Z^+| m^- / |Z^-| m^+ \quad (28)$$

$$\sigma^{+-} / \sigma^{--} = \{ \langle j^+(0) j^-(0) \rangle \int_0^{\infty} f(t) dt \} / \{ \langle j^-(0) j^-(0) \rangle \int_0^{\infty} f(t) dt \} = \langle j^+(0) j^-(0) \rangle / \langle j^-(0) j^-(0) \rangle = |Z^+| m^- / |Z^-| m^+ \quad (29)$$

, which means we have numerically confirmed the relation corresponding to (18).

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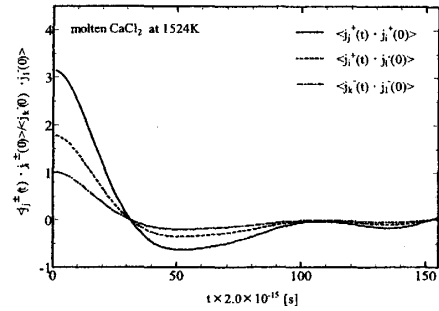


Fig.3 Current correlation functions of molten CaCl_2 at 1524K.

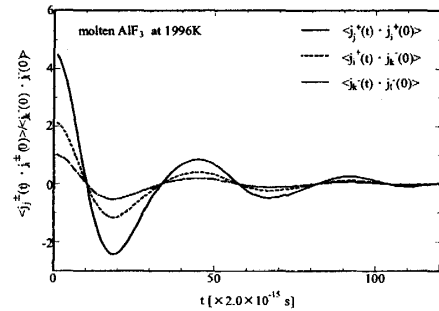


Fig.4 Current correlation functions of molten AlF_3 at 1996K.